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Air Pollution Measurement by Fourier Transform Spectroscopy

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16. ABSTRACT

Fourier transform spectroscopy substantially reduces the limitations on infrared methods of pollution measurement. EPA has used long path cells and Fourier transform spectrometers for pollutant measurement both in the laboratory and in the field. Labile pollutants are best measured in the open air using folded paths of one kilometer or more. Stable pollutants are best measured in miniature folded-path cells after concentration and separation from the main gases in the air. Examples of ambient air pollution measurement are given.

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Air pollution measurement by Fourier transform spectroscopy

Philip L. Hanst

The use of infrared methods in pollution measurement has been hampered by sensitivity limitations and by interferences from water vapor. Fourier transform spectrometer systems reduce these limitations by their high optical efficiency and their ability to manipulate spectra for removal of interfering bands. At the Environmental Protection Agency we have sought to further increase the sensitivity of the infrared technique by evolving optimal long path cell designs and sample concentration techniques. Reactive pollutants such as O_3, H_2O_2, HNO_3, HNO_2, H_2CO, HCOOH, PAN, HCl, NH_3, NO, and NO_2 are best measured in the open atmosphere. In this case one strives toward large absorption cells with the paths as long as practical. Our largest cell is being used to measure pollutants in the smog at Riverside, California. This cell uses an eight-mirror system for multiple-passing radiation along a 23-m base path, yielding total paths measured in kilometers. Reactive gases at levels of just a few ppb have been measured. For measuring nonreactive pollutants, such as hydrocarbons and halocarbons, maximum detection sensitivity is achieved with small folded-path cells rather than with large cells. In this case a pollutant concentrate is prepared and introduced into a miniaturized multiple-pass cell designed for maximum path-to-volume ratio. Cryogenic trapping to separate the pollutants from the major constituents of the air has yielded concentration factors as high as one million. The smallest multiple-pass cell we have built to date encloses a 115-cm light path within a volume of 3 cm^3. This cell when used with the FTS spectrometer and mercury–cadmium–telluride detector permits the detection of nanogram quantities of pollutant gases. Measurements have been made of trace gases in the air at mixing ratios as low as 2×10^{-11}.

Introduction

It is well known that the infrared absorption spectrum can be used to measure nearly every gaseous air pollutant. Infrared applications have been discussed in many previous articles on air pollution measurement.[1–4] In actual practice, however, the infrared technique has not been extensively applied to the measurement of the ambient air. Among the major pollutants, only carbon monoxide is commonly measured by infrared. Surveys of measurement methods demonstrate the small utilization of the infrared techniques.[5,6] In the case of sulfur dioxide, for example, the survey by Lawrence Berkeley Laboratory listed fifty-four different instruments as being available for measurement of SO_2 in the ambient air, none of which used the infrared bands. Nitrogen oxides are another example; in spite of their highly structured infrared bands, NO_2 and NO are nearly always measured by observing the chemiluminescence produced in their reaction with ozone. Similarly, ozone is measured by its chemiluminescence in reacting with ethylene. Formaldehyde has been measured by the purple color produced in its reaction with chromatropic acid reagent. Hydrocarbons are measured by flame ionization. Hydrogen chloride is measured by its reaction on basic filter paper. Since all these cases of pollution measurement are amenable to the techniques of infrared spectroscopy, the infrared method must be examined critically to see what limitations have prevented its adoption.

It is clear that the two main limitations of the method are as follows: (1) when the air is examined in the commercially available absorption cells the pollutants show only very weak absorption bands; and (2) the absorption lines of atmospheric water vapor dominate the air spectrum and interfere with pollutant detection. Fourier transform infrared spectroscopy has been found to minimize both of these limitations.

Detectability Limits

The small absorption limitation and the means of overcoming it are both illustrated by the radiation absorption equation $\ln I_0/I = k_\nu \cdot L \cdot P$. I_0 is the intensity of radiation (at frequency ν) incident on the air sample, I is the intensity of light transmitted through the sam-

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ple, k_ν is the absorption coefficient of the sample at the frequency being considered, L is the pathlength of radiation through the sample, and P is the partial pressure of the absorbing gas. Let it be assumed that an analyst wishes to see a peak in his spectrum that has a maximum absorption of 10%. Then, $\ln I_0/I = 0.1$. Knowledge of both the absorption coefficient and the available pathlength then allows calculation of the required partial pressure of absorbing gas. For example, the ozone band near 1050 cm^{-1} has a peak absorption coefficient of about 10 $atm^{-1}\,cm^{-1}$. A laboratory 10-cm cell would therefore need to contain 10^{-3} atm of ozone to give the 10% maximum absorption. An air pollution chemist would more likely be interested in measuring about 10^{-8} atm of ozone, so he would require a sensitivity improvement by a factor of 100,000. For other pollutants, even larger improvement factors would be desired.

For any pollutant it is obvious that the detection sensitivity will be increased if the noise in the spectrum is reduced. This is where Fourier transform spectroscopy shows one of its major advantages over the older spectroscopic methods. The high optical throughput of the interferometer, the high degree of multiplexing during detection, and the availability of cryogenically cooled detectors all have reduced the noise level in the spectrum and have made it possible to see much weaker absorption bands than could be seen with earlier instruments. This has been discussed previously.[2]

It was reported in the earlier paper that a Fourier transform spectrometer with a mercury–cadmium–telluride detector operating through a long path absorption cell had shown a signal-to-noise level of 2000. This meant that a value of $\ln I_0/I = 0.0005$ would yield a detectable band or line. This was an improvement of a factor of 200 over the 10% absorption example given above, moving the 10-cm cell detectability level for many gases down to a few microatmospheres. The required further gain of several orders of magnitude needed for ambient pollution measurement was achieved through the use of a multiple pass absorption cell with 432-m total path. This reduced the detectable level of many pollutant gases to the order of 10^{-9} atm. This ppb sensitivity only applied to those pollutant gases whose bands fell outside the spectral region of heavy absorption by water vapor. Although water interference was reduced by plotting the ratio of the polluted air spectrum over the spectrum of properly humidified reference air, the detection limits for the major pollutants SO_2, NO_2, and NO still did not reach the ambient air levels. To detect those compounds it appears necessary to partially dry the air.

Additional means of increasing detection sensitivity are now considered for two classes of pollutants. Class 1 includes those pollutants that cannot easily be separated from the major constituents of the air—such as the reactive gases ozone, hydrogen peroxide, peroxy acetyl nitrate, formaldehyde, and nitric oxide and the water soluble gases nitric acid, formic acid, nitrous acid, nitrogen dioxide, and ammonia. This class of pollutants must be measured on a undisturbed sample of air. Class 2 includes pollutants that can be separated from the major constituents of the air—such as hydrocarbons and the chlorofluorocarbons. In this case large gains in detection sensitivity can be achieved by sample concentration.

Technique for Class 1 (Labile) Pollutants

For measuring the labile pollutants in the ambient air a large and very long absorption cell is required. The multiple-pass cell mentioned above was tested at a path of 417 m in the smog at Pasadena, California, in 1973.[7] The cell gave measurements of ozone, peroxy acetyl nitrate, formic acid, methanol, carbon monoxide, various hydrocarbons, and several halocarbons. This large cell did not, however, reveal the presence of nitric acid or formaldehyde, each of which was expected to be present at levels of a few ppb. A realistic appraisal of the signal-to-noise level in the spectra and of the difficulties of removing water vapor interference led to the conclusion that 10 ppb of HNO_3 and 15 ppb of H_2CO could have gone undetected. While it served a good purpose to place these upper limits on the amounts, it would have been considerably more useful (and more satisfying) to actually have measured the amounts of HNO_3 and H_2CO. Thus the 417-m multiple-pass cell, which had a base path of 9 m, still was not large enough. It was therefore decided to continue the work with larger mirrors in a cell with a longer base path.

A larger cell capable of operating at total paths of 1 km or greater was put into operation in 1976 at Riverside, California. The cell is operated by the Statewide Air Pollution Research Center under an EPA research grant. This system is now measuring the HNO_3 and H_2CO as well as many other pollutants.[8]

Figure 1 depicts the multiple reflection cell and FT-IR spectrometer. The multiple reflection optics follow the eight-mirror plan described in an earlier article.[2] Four rectangular mirrors, cut from a single 41-cm diam Pyrex blank, comprise the in-focus end of the cell at the spectrometer. Three of these mirrors are 6.4 cm wide and 32 cm long, while the fourth is slightly shorter (28 cm) to provide the entrance and exit apertures for the infrared beam. The assembly of collecting mirrors consists of four 30-cm diam round mirrors which are 22.5 m from the rectangular mirrors. All mirrors are optically polished and gold-coated for maximum reflectivity in the infrared.

The cell housing consists of a sectional rectangular aluminum frame (total dimensions: $0.81 \times 0.84 \times 23$ m) enclosed at the bottom and one side with Plexiglas and with 50-μm FEP Teflon on the other two faces. Teflon was used for the two sides most exposed to the sun to provide good transmission of solar radiation when the cell is being used as a reaction chamber for synthetic systems. A removable sun screen can be installed (not shown in Fig. 1) over the entire length of the cell to reduce thermal effects on the stability of the infrared

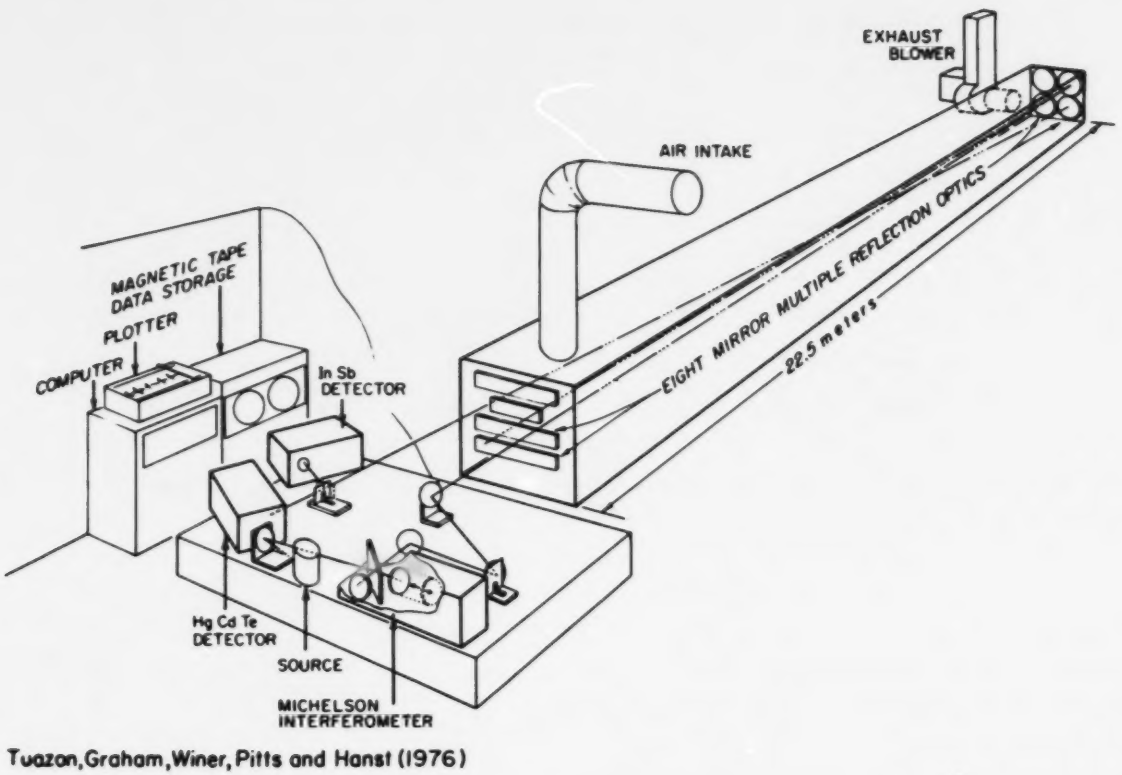

Fig. 1. Kilometer pathlength FT-IR system.

beam during ambient monitoring. To minimize vibrations, the mirror assemblies are each mounted on platforms completely independent of the cell housing.

Coupled with the cell is a Digilab interferometer system housed in a 3.7 × 3.7-m air-conditioned building. The collimated infrared beam from a Nernst glower is modulated by a Digilab model 296 Michelson infrared interferometer capable of spectral resolution as high as 0.5 cm^{-1} and is imaged at the entrance aperture of the cell. The beam exiting from the cell is sent to either of two liquid N_2 cooled detectors: a photovoltaic InSb detector for the 2000–3900-cm^{-1} range or a photoconductive HgCdTe detector for the 600–2000-cm^{-1} region. Data collection and processing are performed by a Data General Nova 1200 computer with 4096 16-bit words of core. A disk unit (128K words) is used for software storage and partial storage of data. Archival data storage of both raw interferograms and computed spectra is provided by a Kennedy model 9700 magnetic tape unit. The Digilab system is also equipped with a Houston Instrument pen plotter, an oscilloscope, and a teletype.

The instrumentation was set up on the roof of the Webber Hall East building on the U.C. Riverside cam-

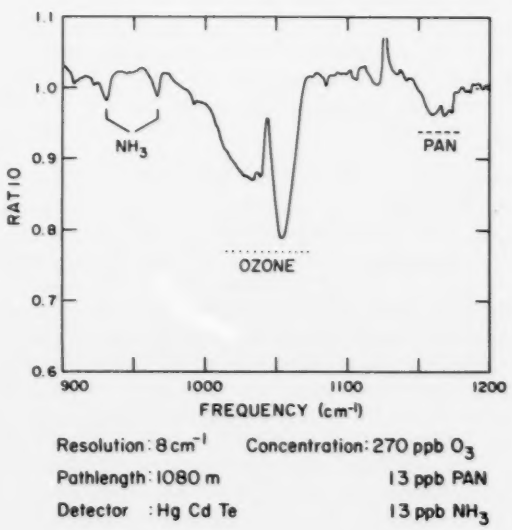

Fig. 2. Riverside ambient air spectrum at 2-cm^{-1} spectral resolution, 1080-m pathlength; 5 October 1976 at 4:34 p.m.; 285-ppb O_3, 13-ppb PAN, 13-ppb NH_3 (HgCdTe detector).

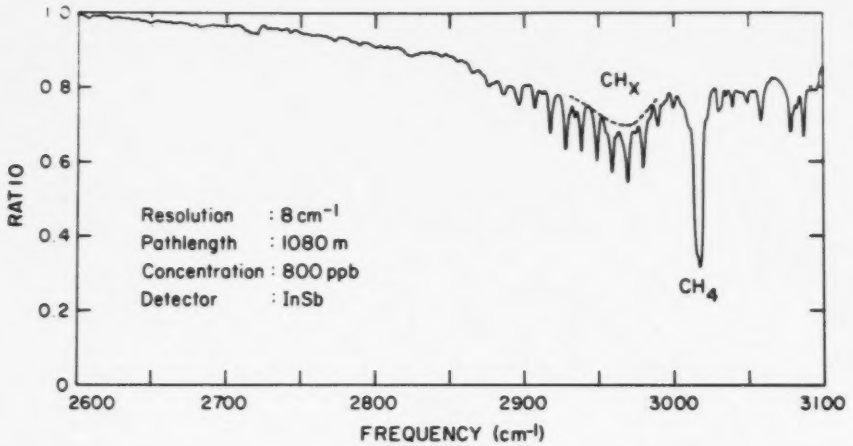

Fig. 3. Riverside ambient air spectrum at 2-cm^{-1} spectral resolution, 1080-m pathlength; 4 October 1976 at 5:43 p.m.; 800-ppb CH_x (InSb detector).

pus. This location is 24 m above the ground and provides unobstructed exposure to prevailing winds from the west, north, or south. No ventilation ducts or exhaust blowers are located on this roof. During ambient monitoring, an atmospheric sample is drawn continuously through the cell at a rate of 330 l/sec^{-1} (one cell volume every 50 sec) by a 1/4-hp blower at one end. Air enters the other end of the cell through a 36-cm diam pipe with an intake 2 m above the roof. Figures 2 and 3 show in ratio plots the detection of several pollutants in the smog in early October 1976. Figure 4 illustrates the detection of nitric acid. This latter figure emphasizes the necessity of using the ratio technique to remove the water vapor interference. Further details on the operation of the system and on the early results were reported in Ref. 8.

Technique for Class 2 (Stable) Pollutants

Stable gases such as hydrocarbon and halocarbon vapors may be separated from the air before being placed in an absorption cell. This separation allows great gains in detection sensitivity. The separation technique used in the EPA laboratory has been cryogenic condensation followed by distillation. A chemical step has also been used to remove CO_2 from the distillate. The first application of the cryogenic method in the measurement of fluorocarbons, carbon tetrachloride, carbonyl sulfide, and other atmospheric trace gases has been described in an earlier publication.[9] Recent refinements of the method will be described here.

A simple collection technique has been used. Air is driven by a pump into a closed vessel immersed in liquid nitrogen. Condensation takes place until the vessel is full, after which the oxygen and nitrogen are pumped off, leaving a residue of ice, solid CO_2, and condensed trace gases.

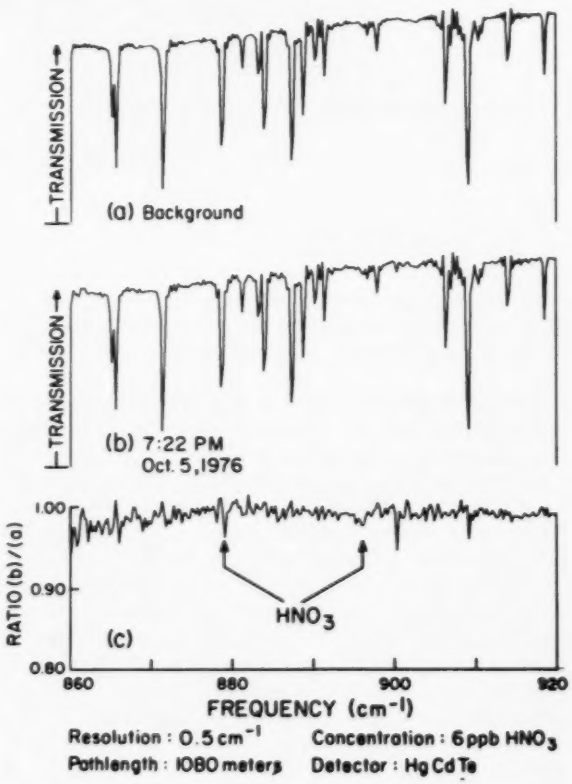

Fig. 4. Riverside ambient air spectrum (5 October 1976 at 7:22 p.m.) at 0.5-cm^{-1} spectral resolution, 1080-m pathlength. Nitric acid concentration, 6 ppb.

The method depends on the vapor pressure–temperature relations as shown in Fig. 5. The most volatile pollutant in the air is CO, as shown by the vapor pressure line at the top of the figure. The CO will condense and distill with the oxygen and nitrogen without separation. This is probably true of NO as well, unless in the condensed phase the NO is oxidized to NO_2.

Methane is next down the scale in volatility. At liquid nitrogen temperature its vapor pressure is approximately 0.01 atm. This is low enough for separation.

Toward the end of the distillation, when the nitrogen and oxygen were nearly gone, a methane-rich fraction then distilled. The spectra showed that during removal of the methane-rich fraction there was no appreciable removal of carbon dioxide, nitrous oxide, or other minor constituents of the residue. Even ethylene remained in the cryocondenser during methane removal.

Ethylene is the most volatile of the nonmethane hydrocarbons, with a vapor pressure of about 2×10^{-6} atm at liquid nitrogen temperature. Nevertheless, spectra recorded during distillation have shown that ethylene is fully retained in the residue as long as the distillation is not carried very far beyond the methane removal stage.

Acetylene, carbon dioxide, nitrous oxide, halogenated compounds, and all other minor molecular constituents of the air do not vaporize from the cryocondenser during the distillation of nitrogen and oxygen.

Nitrous oxide serves as an inherent calibration of the degree to which the concentrations of trace gases have been raised by the condensation and distillation process. N_2O occurs everywhere in the lower atmosphere at a mixing ratio of 3×10^{-7}. Since the vapor pressure of N_2O at liquid nitrogen temperature is less than 10^{-9} atm, all the N_2O will remain with the other trace gases until final removal from the cryocondenser. Because of its inertness, the N_2O will behave in handling like the hydrocarbons, halocarbons, and other inert pollutants. When the infrared spectrum is finally recorded, the strength of the N_2O bands in the spectrum will tell how much gain in pollutant concentration was obtained through the condensation. In other words, the N_2O bands gave the spectrum amplification factor.

In the early trials of the technique, the collected residue was vaporized from the cryocondenser into the infrared absorption cell with no attempt to remove CO_2. This produced an infrared spectrum dominated by CO_2 lines which tended to obscure the bands of other trace gases. One way to minimize the interference is to plot a ratio of the spectrum of the residue over a spectrum of pure CO_2. Unfortunately it has been found that in such a plot the strong absorption causes some parts of the spectrum to be lost and others to be rendered unduly noisy. It is better to remove the CO_2, providing that other trace gases are not removed.

Sodium hydroxide has been found effective in removing CO_2 without disturbing most of the other gases. Halocarbons, hydrocarbons, nitrous oxide, and carbonyl sulfide, for example, are not taken up by the NaOH during CO_2 removal.

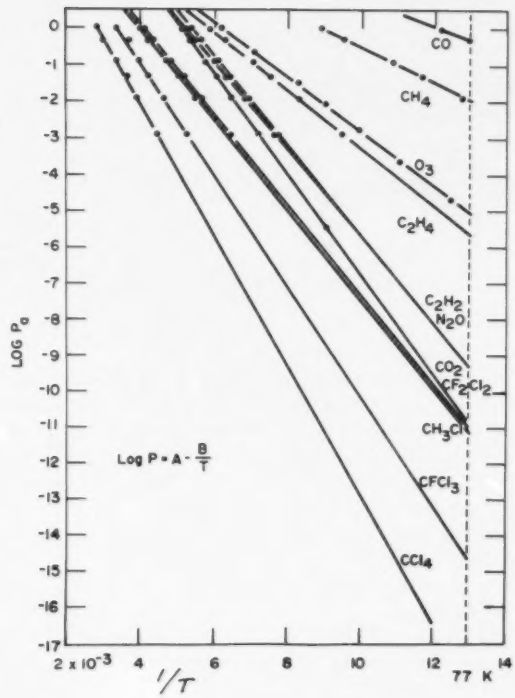

Fig. 5. Vapor pressure–temperature plots.

A second limitation of CO_2 is that it holds down the spectrum amplification factor. If the collected residue with CO_2 present is placed in an infrared absorption cell at a total pressure of 1 atm, the gas will consist mainly of CO_2 whose concentration has been raised from its normal 0.00033 atm to 1 atm—an amplification factor of 3000. If the CO_2 is removed, however, the N_2O becomes the most prevalent gas in the mixture, allowing a maximum amplification factor of 3.3×10^6. The maximum amplification factor obtained in experiments so far has been approximately 1×10^6.

When the collected residue is placed in an infrared cell large enough to hold it all, it is the path-to-volume ratio of the cell that determines the strength of the infrared band, rather than the total pathlength. Small, compact cells are more efficient than large cells. In our recent work we have used a new and novel variation of White's original multiple pass cell.[10] This variation has allowed us to miniaturize the White cell without using a complicated microassembly of parts. We have used the three-mirror configuration, but with the two collecting mirrors placed one behind the other rather than side by side. This allows us to have each of the three mirrors mounted in its own spherical glass joint. Each mirror can then be aimed individually by rotating the ball joint. When alignment is obtained, the joints are cemented in place.

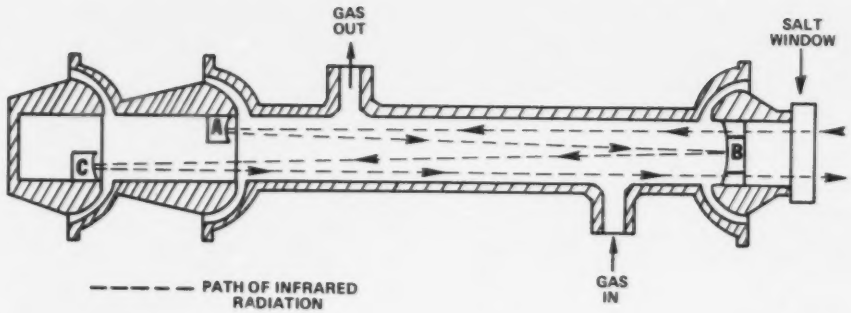

Fig. 6. Multiple-pass cell with ball joint mounting of mirrors.

The configuration of mirrors and ball joints is shown in Fig. 6. The radius of curvature of the single mirror B falls at a point midway between the dual mirrors. The focal points of mirrors A and C are, respectively, behind and in front of mirror B. The positions of the foci near B compensate each other, and the cones of light maintain their integrity through a large number of passes. In appearance, the images on the surface of mirror B are difficult to distinguish from perfectly focused images.

The smallest ball joint cell we have made uses the 18/9 standard joints, which is to say that the i.d. of the glass cell is 9 mm. The miniature (9-mm high) focusing mirrors were cut from a single small mirror that had a 36-mm radius of curvature. When used at 32 passes this microcell had a path of 115 cm folded in a volume of 3 cm^3. Optical throughput was sufficient to give low noise spectra of the kind illustrated in Fig. 7.

The path-to-volume ratio of about 38 for this microcell compares with a path-to-volume ratio of about 0.3 for multi-pass cells that are now available commercially. Thus the amount of gas needed for a measurement has been reduced by a factor of more than 100. For example, in this microcell about 15 ng of ammonia will give 3% absorption maxima at 935 cm^{-1} and 970 cm^{-1} similar to those shown in Fig. 2.

Figure 7 shows an example of the detection power of the Fourier transform spectrometer when used in conjunction with the cryogenic concentration technique and a miniaturized multiple pass cell. The cell in this case was not our smallest. It was an intermediate size, with a path of 1100 cm folded inside a volume of 200 cm^3, giving a path-to-volume ratio of 5.5. The spectrum between 700 cm^{-1} and 1200 cm^{-1} shows identifiable bands of eleven species of pollutant in addition to the naturally occurring nitrous oxide. Carbon dioxide was removed from the gas mixture by NaOH. The amplification factor indicated by the strength of the N_2O band is approximately 16,000. It is therefore calculated that approximately 3 m^3 of air were condensed and distilled to yield the residue that produced the spectrum.

Figure 7 also shows the great value of the spectrum subtraction routines that are available with the Fourier transform spectrometer system. In the lower spectrum the dominant bands obscure the weaker bands. In the upper spectrum, however, the dominant bands of

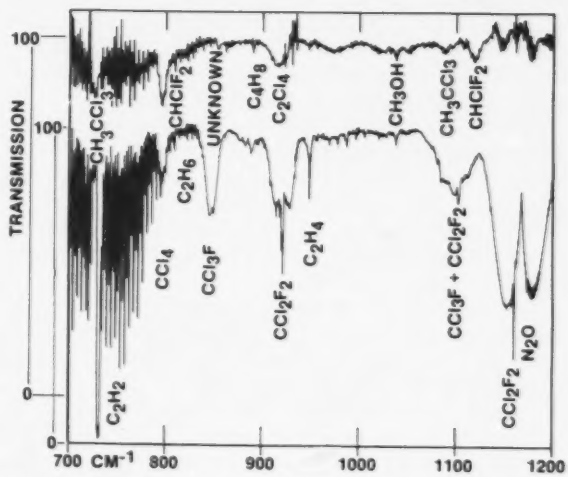

Fig. 7. Pollutant spectra obtained with aid of cryogenic concentration technique: Lower—condensate from outside air at Research Triangle Park, 22 October 1976 (weather: clear)—11-m cell. Upper—condensate spectrum after subtraction of bands due to C_2H_2, C_2H_4, CCl_3F, CCl_2F_2, and N_2O.

Table I. Mixing Ratio of Gases in Original Air Sample [a]

N_2O	3×10^{7} (assumed)	CCl_4	1.2×10^{-10}
C_2H_6	4×10^{-9}	CH_3CCl_3	1×10^{-10}
C_2H_2	2×10^{-9}	C_2Cl_4	1×10^{-10}
C_2H_4	4×10^{-11}	CH_3OH	4×10^{-11}
CCl_2F_2	2.6×10^{-10}	$CHClF_2$	4×10^{-11}
CCl_3F	1.7×10^{-10}	C_3H_8	2×10^{-11}

[a] From Fig. 7.

acetylene, trichlorofluoromethane, dichlorofluoromethane, ethylene, and nitrous oxide have been subtracted, revealing the weaker bands of other pollutants and allowing them to be measured. Table I gives the calculated mixing ratios for the gases in the original air sample.

It is obvious from the table that an extremely high degree of analytical sensitivity is obtained when the Fourier transform infrared method is combined with appropriate methods of sample preparation. The example also shows that in many aspects of air analysis, gas chromatographic separations are not required. The subtraction technique will generally suffice for the unraveling of complex spectra.

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